

MINIATURE, HIGH-RESOLUTION, QUADRUPOLE MASS SPECTROMETER ARRAY

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ABSTRACT

A miniature quadrupole mass-spectrometer array consisting of 16 rods in a 4 X 4 array is reported. Each rod is 25 mm long and 2 mm diameter. The ionizer is of a miniature Nier-type design, and the detector is a channel type electron multiplier. Operating frequencies are 5.3 MHz, 7.1 MHz, and 12.9 MHz. The mass range demonstrated herein is 1-300 amu; and the resolution of the system is 0.1-0.5 amu (FWHM), or $m/\Delta m = 600$. The present sensitivity is calculated and measured to be approximately 1×10^2 counts/torr-sec.

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1. INTRODUCTION

The quadrupole mass spectrometer has become one of several standard laboratory and commercial instruments for use as in chemical analysis, environmental monitoring, and as a residual gas analyzer. It is also one of the most frequently flown instruments for planetary aeronomy studies, and should find increasing use in planetary surface studies and geological ageing [1]. In order to realize NASA's goal of having "faster, better, cheaper" space missions, one must as a corollary examine "smaller" instruments in order to reduce mass, volume, and power. These commodities ultimately translate into size of the launch vehicle, the science-platform power system, and the budget. In any long-duration human flight mission, such as a mission to Mars, it is essential to apportion these commodities in a deliberate way.

Described herein is a miniature quadrupole mass spectrometer array in which the ionizer, rods, and detector regions were scaled downwards in size in such a way that mass range and resolution were not sacrificed, and the sensitivity was held comparable to that of its larger commercial cousins. The quadrupole mass-spectrometer array consists of 16 rods in a 4 x 4 array to form nine separate quadrupolar regions. The ionizer is of a miniature Nier-type design, and the detector is a channel-type electron multiplier. The overall sensitivity to positive-ion detection is approximately 1×10^{12} counts/torr-sec. The demonstrated mass range is 1-300 amu, with a resolving power of $m/\Delta m \approx 600$. This corresponds to a resolution of

0.1-0.5 amu (FWHM). The unit is approximately 7 cm in length and 3 cm diameter, including separate shields around the rod array and the detector. Total system mass with shields is approximately 30 grams.

The present embodiment of the quadruple array differs from that of Ferran and Boumsellek [2] in the following significant ways: (a) the quadruple rods herein are positioned, using carefully-machined ceramic positioning jigs, to a 0.1 % dimensional tolerance, hence allowing resolutions of better than 0.5 amu (full width at half maximum, FWHM), and excellent spectral wings at the 0.1 FWHM level, (b) all dielectric surfaces are plated with a conducting material (here, titanium) to prevent surface charging, (c) electrical contacts to the rods are rigidly spot-welded to each rod using the symmetry of the poles, with no possibility of distorting the positional accuracy of the rods, (d) detection herein can be by means of either a channel-type multiplier or Faraday cup, and (e) the quadruple and detector regions are separately shielded to reduce backgrounds from ions, electrons, and photons [31].

In Sec. II is outlined the methods used to fabricate the quadruple array, and the radiofrequency circuitry used to demonstrate its operation. Mass spectra and sensitivity results are presented in Sec. III.

II. EXPERIMENTAL METHODS

A. Mass Filtering

The basic methods of quadrupole mass spectrometry have been presented in the works of Paul, *eta/*. [4][5]. For a voltage Φ on alternate rods given by $\Phi = U + V \cos \omega t$, one set of rods would carry potential $+\Phi$ and the alternate set $-\Phi$. Here, U is the *dc* potential, V the peak amplitude of the harmonic component, and ω is the operating frequency of the array. For the case of hyperbolically-shaped rods, standard expressions for U and V are given in terms of the reduced Mathieu parameters a and q by,

$$a = -\frac{8eU}{mr_o^2\omega^2}, \quad q = \frac{4eV}{mr_o^2\omega^2}, \quad (1)$$

Here, m/e is the particle mass-to-charge ratio, r_o is the radius of the inner circle tangent to the four pole faces, and ω is the angular frequency. The “ideal” mass resolution is realized when only a single mass m is present within the (a, q) region of stable Mathieu ‘orbits. Values of this point in the diagram are given by $a = 0.237$, and $q = 0.706$. In terms of convenient laboratory parameters (m in amu, f in MHz, r_o in cm) one can rewrite Eq. (1) as,

$$U = 1.213 mf^2 r_o^2, \quad V = 7.223 mf^2 r_o^2. \quad (2)$$

These values of U and V are linearly ramped to bring successive masses into the

stability region. The ratio U/V is maintained at 0.168 for optimal resolution. Values of other parameters chosen here were $r_o = 0.0862$ cm, and $f = 5.3$ MHz, 7.1 MHz, or 12.9 MHz. The diameter of the cylindrical rods used here was taken as 1.16 times the distance $2r_o$ of closest approach of the hyperbolic rods. The accessed mass range was $m = 1-300$ amu (Sec. III).

B. Mechanical Assembly

The strategy employed in the present design of the miniature quadrupole system was to reduce the size of a quadrupole to one having 25.00 mm-long rods, and to use the concept of an array of rods [41][61]. If one shrinks the size of any system by a factor of, say, k (k less than unity), then the volume will shrink by k^3 , the mass by somewhat less than k^3 (due to dead space), and the input aperture area (hence sensitivity) by k^2 . In order to compensate for the lost aperture area, one can assemble a $k \times k$ array of mass filters, all working in parallel. One then regains the lost sensitivity by the relation $k^2(\text{shrinkage}) \times k^2(\text{array}) = 1$, and still reduces mass and volume by roughly a factor k . Additionally, as pointed out earlier [4], one utilizes the power supplied to the rods more efficiently, since in a $k \times k$ array each rod can supply electric field intensity to as many as eight neighboring rods, whereas in a 2×2 array only three neighbors are available for sharing [4]. As a result, the power required to drive nine quadrupolar regions is not nine times that of a single region, but rather 4.5.

Critical to the proper operation of a quadrupole mass filter is the machining precision of the rods and their alignment. In order to highlight this criterion, a brief review is given of the required precision as a function of desired mass and mass resolution. Let r_o^+ and r_o^- represent upper and lower limits, respectively, to the radius of each quadrupole rod. For a fixed dc potential U and frequency f the transmitted masses due to the different radii will be [Eq. (2)],

$$\begin{aligned} U &= 1.213 f^2 (r_o^+)^2 \sqrt{m - \frac{\Delta m}{2}}, \\ U &= 1.213 f^2 (r_o^-)^2 \sqrt{m + \frac{\Delta m}{2}}. \end{aligned} \quad (3)$$

Using the expressions for r_o [Eq. (2)], r_o^+ , and r_o^- [Eq. (4)] one may obtain an expression for the relative dimensional tolerance (in percent) as,

$$\frac{r_o^+ - r_o^-}{r_o} = 100 \left[\sqrt{\frac{m}{m - \Delta m/2}} - \sqrt{\frac{m}{m + \Delta m/2}} \right]. \quad (4)$$

For $\Delta m/m \ll 7$, Eq. (4) can be approximated as $100(\Delta m/2m)$. The family of curves of Eq. (4) is plotted as a function of both m and Δm in Fig. 1. One may select a desired resolution Δm , the mass m at which that resolution is desired, then read off the required dimensional tolerance. To obtain, for example, 0.5 amu resolution at $m = 250$ one requires a dimensional tolerance of about 0.1 %. This was the tolerance adhered to in the present work. Moreover, the tolerances from Fig. 1 are probably pessimistic, since all the rods were assigned the same deviation. The effect of having only one or two rods misaligned would affect the resolution less.

In the present case, a 4 x 4 array of rods was used, with rods lengths of 25.00 mm and diameter 2.000 mm. The rods material was 316 (nonmagnetic) stainless steel. Each individual rod was ground true and straight to a precision of 0.05% or better. In order to maintain the 0.1 % dimensional tolerance in the placement of the 16 rods, the rods were mounted in two machinable ceramic (Corning Macor[®]) jigs, one at each end of the rods. In each jig was machined 16 holes of 2.000 mm dia placed in a square array on 3.724 ± 0.0004 mm (± 0.1 %) centers. Nine additional holes were provided for entry and exit of the ions, and four holes for larger-diameter mounting rods to sandwich the structure in place. A system view is shown in Fig. 2. In order to prevent surface charging of the ceramic insulators, both the front (facing the ion stream) and back surfaces were plated with titanium, as well as the interior of the nine holes to allow passage of the ions. A small halo of bare ceramic was left around each rod in order to provide radiofrequency (*rf*) and direct-current (*dc*) electrical insulation between the rods. Electrical contact was made at the back surface of the exit jig by spot-welding stainless steel strips to alternate rods. By thus taking advantage of the quadruple symmetry, only two leads had to be brought through vacuum.

C. Ionizer and Optics Assembly

The ionizer consisted of a spiral-wound 0.04 mm-dia iridium-tungsten filament. The filament center was biased at -70V relative to ground, and electrons from the

filament were accelerated into the ionizer can held at ground potential. Typical emission currents used were 0.3-1.0 mA. A repeller plate was used to eject positive ions towards a decelerator lens, and then into the grounded entrance aperture. This aperture consisted of nine 0.26 mm-dia holes, each registered to the center of its respective quadrupole to a dimensional tolerance of $\pm 0.1\%$. After the mass filter ions exited nine 1.006 mm-dia holes in the machinable ceramic jig. Each hole was coated internally with titanium. Ions were then accelerated by an aperture lens and focused into the front cone of a small channel-type electron multiplier. Pulses from the multiplier were preamplified, discriminated, amplified, then stored in a multichannel scaler as a function of *rf* ramp voltage.

D. Electronics

The basic philosophy of the electronics design is similar to that used by Paul, *et al.* [41], and in commercial quadrupole mass spectrometers [7], but modified for operation at 5.3 MHz, 7.1 MHz, and 12.9 MHz. A schematic of the electronics is shown in Fig. 3. The output of a programmable high-frequency power supply constitutes the primary windings *P* of an air-core transformer. The two secondary windings *S*⁺ and *S* are wrapped one-to-one with respect to *P*, and power the positively- and negatively-biased sets of rods, respectively. The *dc* bias potential *U* is extracted from a point of the secondary windings *S*⁺, *S* having roughly 1/6th ($= U/V$) the total potential across *S*⁺ or *S*. This fraction is then half-wave rectified by

diodes D , and filtered through capacitors $C3$. For fine-tuning the ratio U/V a portion of the dc potential is used to bias the $R2$ -diode D legs through the variable resistors $R5$. More sophisticated lower-frequency versions of this basic design have been built elsewhere with, for example, a quartz crystal-based oscillator which is buffered from the primary windings [7].

III. RESULTS AND DISCUSSION

Presented in this section are representative mass spectra taken with the 4 x 4 array. All spectra were taken at a fixed electron energy of 70 eV. Gaussian fits (shown as solid lines in the figures) were made, and the resolutions quoted are the FWHM of these fits. Tests of mass range and resolution were first run using the rare gases and their isotopes. Shown in Figs. 4-6 are mass spectra of argon, krypton, and xenon taken at a resolution of 0.5 amu (FWHM) and covering the mass range 36-136 amu. In order to test the analyzer to higher masses a sample of C_6F_{12} (dodecafluoro-dimethylcyclobutane, molecular weight 300) was run. A mass spectrum, with identification of the more intense features, is shown in Fig. 7.

The operating frequency in Figs. 3-6 was $f \approx 5.3$ MHz. In order to obtain resolved spectra for the lighter, faster ions in the range $m \approx 1-4$ amu a higher oscillator frequency of 12.9 MHz was selected. Results are shown in Fig. 8 for a mixture of H_2 and tie. The atomic and molecular masses are resolved with widths

of 0.1 and 0.2 amu (FWHM). The H^+ peak is also well-separated from the “zero blast” peak at zero *dc* voltage where the quadrupole mass analyzer acts as a high-pass filter. An additional mass spectrum in the range 1-40 amu for an H_2 - He - N_2 - Ar mixture is given in Fig. 9. The operating frequency here was 7.1 MHz,

Finally it is interesting to provide an estimate of the sensitivity of the quadrupole array, as calculated from a combination of measured and estimated quantities. The number of ions N_i produced per second can be related to experimental parameters by,

$$N_i(\text{sec}^{-1}) = n_i \epsilon_Q \epsilon_{CEM} A R , \quad (5)$$

where n_i is the density of ions produced in the Nier ionizer, A is the calculated geometrical open area of the nine entrance apertures (0.05), ϵ_Q is the transmission efficiency of the quadrupole for the tuned ion (1.0), ϵ_{CEM} is the detection efficiency of the channel-type multiplier (0.8), and R is the maximum count rate of the ion multiplier (2×10^5 Hz). The ion density n_i can in turn be related to the ionization parameters in the source and is given by,

$$n_i = n_e \sigma_i / n_o . \quad (6)$$

Here, n_e is the electron density (approximately $2 \times 10^{16} \text{ cm}^{-3}$, corresponding to a 1 mA beam of 0.5 cm diameter at 70 eV energy), σ_i the ionization cross section ($3 \times 10^{-16} \text{ cm}^2$), l the electron-neutral interaction path length (5 mm), and n_o the neutral target density in the source. With the values given above one has $N_i = 8.0 \times 10^{-5}$

n_o . In terms of the neutral target pressure, this become $N_i(\text{sec}^{-1}) = 3 \times 10^{12} P(\text{torr})$. This estimate compares favorably with the measured sensitivities for eight species (H^+ to Xe^+). These measurements were made by filling the entire vacuum chamber to a known pressure of target gas, then measuring the count rate of positive-ion signals through the system with known values of electron current. The results of these measurements for the eight species H^+ , H_2^+ , He^+ , N^+ , N_2^+ , Ar^+ , Kr^+ , and Xe^+ gave sensitivities in the range $(0.2 - 2.7) \times 10^{12}$ counts/torr-sec, in good agreement with the above estimate.

Improvements sensitivity are possible to the arrangement of Fig. (2). The most obvious one is to increase the number of parallel rods to increase the geometrical aperture area A in Eq. (5) above. An increase to a dimension $n = 8$, for an 8×8 array, would increase the number of quadrupolar regions from $(4-1)^2$ to $(8-1)^2$, or a factor of 5.4 increase in sensitivity. Equally as important, three-dimensional, space-charge limited fields-and-trajectories calculations of the present Nier design show that not all apertures are fully covered by the electron beam [8]. Preliminary results show that (a) the coverage of the apertures by electrons can be improved, and (b) extraction of the ions using the field penetration of an additional lens after the ionization region (Fig. 2) can also be improved. These developments are presently under way.

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FIGURE CAPTIONS

Figure 1. Relative dimensional tolerance (in percent) required to obtain a desired mass resolution Δm (FWHM) at a mass m [Eq. (4)]. Curves are labeled by the value of desired resolution Δm .

Figure 2. View of the various components of the miniature quadrupole array. Shown are a miniature Nier-type ionizer (A), 16 rods in a 4 x 4 array (B) positioned with ceramic jigs (C) at each end, and a channel-type ion detector (D).

Figure 3. Schematic of the basic electronics used to power the rods array.

Figure 4. Mass spectrum of the Ar^+ isotopes at 36, 38, and 40 amu. The operating frequency here is 7.1 MHz.

Figure 5. Mass spectrum of the Kr^+ isotopes at 78, 80, 82, 83, 84, and 86 amu. The operating frequency here is 7.1 MHz.

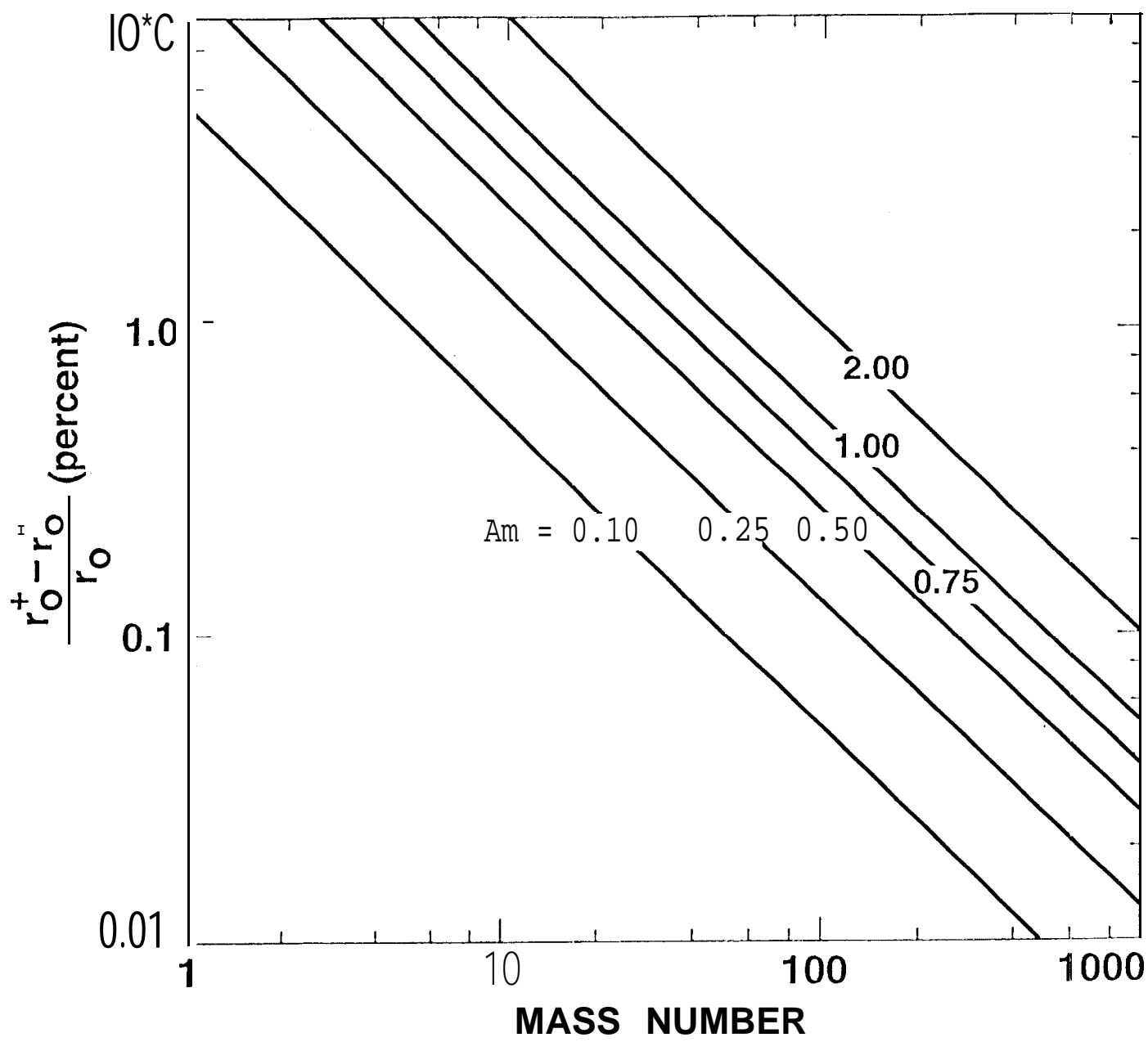
Figure 6. Mass spectrum of the Xe^+ isotopes at 124, 126, 128, 129, 130, 131, 132, 134, and 136 amu. The operating frequency here is 5.3 MHz.

Figure 7. Mass spectrum of C_6F_{12} (dodecafluorodimethylcyclobutane) in the range

38 (F_2^+)—300 ($C_6F_{12}^+$) amu, illustrating the higher mass range of the quadrupole array. Operating frequency here was 5.3 MHz. Based on species mass, reasonable identification of the more intense features are: (a) F_2^+ , (b) F_3^+ , (c) $C_3F_5^+$, (d) $C_6F_8^+$, (e) $C_5F_7^+$, (f) $C_6F_{10}^+$, (g) $C_6F_{12}^+$.

Figure 8. Mass spectrum of a He-H₂ mixture at an operating frequency of 12.9 MHz. The rising portion towards zero mass is the familiar “zero blast.”

Figure 9. Mass spectrum of a H₂ - He - N₂ - Ar mixture at an operating frequency of 7.1 MHz.



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